

# The Ions $\text{MCp}_2^+$ ( $\text{M} = \text{Sc}, \text{La}$ ): Significantly Bent Sandwich Species

Martin Kaupp,<sup>1a</sup> Oleg P. Charkin,<sup>1b</sup> and Paul von Ragué Schleyer<sup>\*1a</sup>

Institut für Organische Chemie I, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Germany, and Institute of New Chemical Problems, Russian Academy of Science, Chernogolovka, Russia

Received May 1, 1992

**Summary:** Ab initio calculations show that the hypothetical organometallic cations  $\text{MCp}_2^+$  ( $\text{M} = \text{Sc}, \text{La}$ ) have bent-metallocene structures. This is due to covalent  $\sigma$ -bonding contributions involving the totally symmetric metal  $d_\sigma$  orbitals, which favor bent geometries. While these orbitals contribute much less to covalent bonding in these systems than the  $d_\pi$  orbitals, their involvement is sufficient to result in bent structures.

Do heavy alkaline-earth-metal and lanthanide(II) metallocenes  $\text{MCp}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}, \text{Yb}$ ) prefer bent or linear sandwich structures?<sup>2-5</sup> While experimental structure determinations indicate bent geometries<sup>2,3</sup> (cf. Figure 1 for the definition of the bending angle), these refer either to gas-phase thermal average structures at elevated temperatures<sup>2</sup> or to solid-state structures where nonnegligible intermolecular interactions are present.<sup>3</sup> Our recent ab initio pseudopotential calculations show that all of these species have very shallow bending potentials.<sup>5</sup> While the calculated equilibrium structures for  $\text{M} = \text{Ba}, \text{Sm}, \text{Eu}$  deviate slightly from linearity,  $\text{CaCp}_2$  and  $\text{YbCp}_2$  probably are linear.<sup>5</sup> These results for the metallocenes contrast sharply with those for simpler  $\text{MX}_2$  species (e.g.,  $\text{X} = \text{halogen}, \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}$ ). The latter show significantly bent structures (except for the lighter metal  $\text{Ca}$ ).<sup>6a-e</sup> Covalent  $\sigma$ -MX-bonding contributions (involving

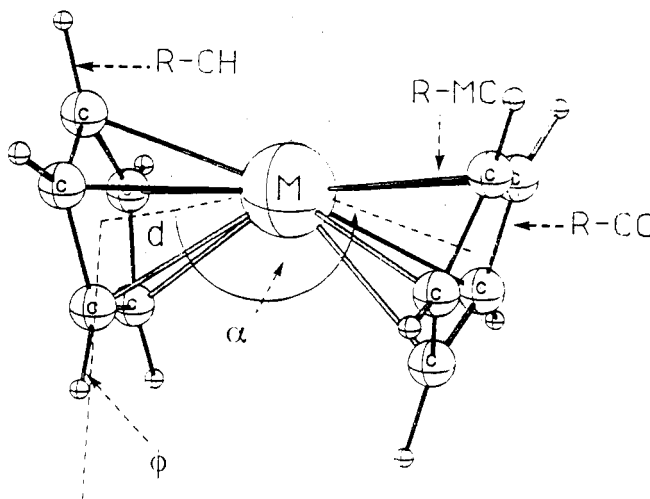


Figure 1. Definition of internal coordinates for  $\text{MCp}_2$  and  $\text{MCp}_2^+$ .

metal  $d$  orbitals) favor bent structures,<sup>6</sup> but  $\pi$ -bonding contributions favor linear  $\text{MX}_2$  geometries.<sup>6d</sup> Since the  $\text{Cp}^-$  ligand functions mainly as a  $\pi$  donor, the reduced preference for bent structures in the  $\text{MCp}_2$  compounds becomes clear.<sup>5</sup>

In addition to these covalent bonding contributions, the polarization of the cation by the anions favors bent structures, whereas the repulsion and polarization of the anions favors linear geometries.<sup>6a,c</sup> Thus, two explanations for the at least slightly bent equilibrium geometries of the heavier  $\text{MCp}_2$  species (e.g.  $\text{M} = \text{Ba}, \text{Sm}$ ) may be envisaged: (a) the polarization of the metal cation by the ligands<sup>2d,5</sup> or (b) the presence of small  $\sigma$ -bonding contributions

(1) (a) Universität Erlangen-Nürnberg. (b) Russian Academy of Science.

(2) (a) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* 1986, 312, C49. (b) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* 1987, A41, 24. (c) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* 1987, 768. (d) Blom, R.; Faegri, K., Jr.; Volden, H. V. *Organometallics* 1990, 9, 372.

(3) (a) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* 1988, 1045. (b) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* 1990, 9, 1128. (c) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* 1984, 106, 4270. (d) Evans, W. J.; Hughes, L. A.; Hanusa, T. P.; Doedens, R. J. *Organometallics* 1986, 5, 1285.

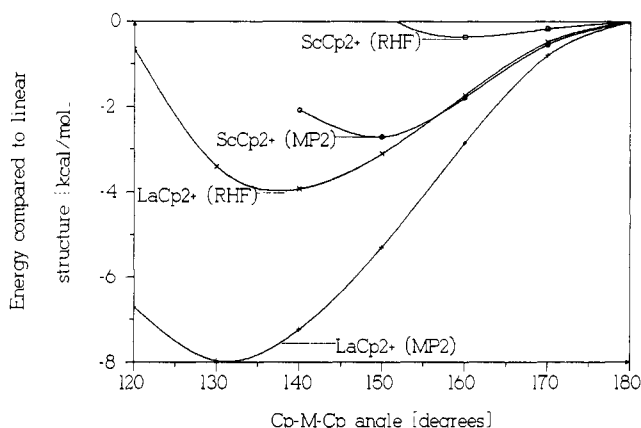
(4) Andersen, A. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rösch, N. *J. Chem. Soc., Chem. Commun.* 1986, 405. Green, J. C.; Hohl, D.; Rösch, N. *Organometallics* 1987, 6, 712.

(5) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.*, in press. For earlier theoretical studies, see refs 2d and 4.

(6) (a) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* 1991, 94, 1360. (b) Seijo, L.; Barandiaran, Z.; Huzinaga, S. *J. Chem. Phys.* 1991, 94, 3762. (c) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* 1991, 113, 6012. (d) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1992, 114, 491. (e) Dolg, M.; Stoll, H.; Preuss, H. *THEOCHEM* 1991, 235, 67. (f) Charkin, O. P.; Djatkina, M. E. *J. Struct. Chem. (Engl. Transl.)* 1964, 5, 415. Charkin, O. P.; Djatkina, M. E. *J. Struct. Chem. (Engl. Transl.)* 1968, 9, 585. Charkin, O. P.; Djatkina, M. E. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* 1969, 12, 2502. Charkin, O. P. *J. Struct. Chem. (Engl. Transl.)* 1973, 14, 355.

**Table I.** M-X Distances R-MX (Å), Bond Length Expansions upon Linearization  $\Delta R_1$  (Å), XMX Angles (deg), and Linearization Energies  $\Delta E_1$  (kcal/mol) for  $MX_2^+$  (M = Sc, La; X = H, F, Cp)<sup>7</sup>

	SCF				MP2			
	R-MX	$\Delta R_1$	XMX	$\Delta E_1$	R-MX	$\Delta R_1$	XMX	$\Delta E_1$
ScH <sub>2</sub> <sup>+</sup>	1.740	0.084	111.9	15.5	1.699	0.091	104.1	24.3
ScF <sub>2</sub> <sup>+</sup>	1.786	0.032	125.8	6.6	1.769	0.037	116.2	11.4
ScCp <sub>2</sub> <sup>+</sup>	2.163	0.003	162.5	0.4	2.104	0.008	149.0	2.8
LaH <sub>2</sub> <sup>+</sup>	2.066	0.154	108.7	28.4	2.020	0.160	106.4	34.7
LaF <sub>2</sub> <sup>+</sup>	2.108	0.055	113.6	13.4	2.090	0.062	108.8	16.6
LaCp <sub>2</sub> <sup>+</sup>	2.590	0.028	138.0	4.2	2.522	0.043	130.7	8.6

**Figure 2.** Bending potentials for  $MCp_2^+$  (M = Sc, La) obtained by SCF and MP2 single-point calculations, respectively.<sup>7</sup>

(dwarfed by the  $\pi$  contributions but still sufficient to cause bending). The isoelectronic systems  $MCp_2^+$  (e.g. M = Sc, La) are expected to be much more covalent than the neutral  $MCp_2$  species, but the trications are less polarizable. Hence, these species are ideal model complexes to differentiate between the two possible explanations: If the complexes are linear, explanation (a) gains credibility for the rather polarizable dications  $Ba^{2+}$  and  $Sm^{2+}$ . If they are bent, this supports the  $\sigma$ -bonding hypothesis (b). We have therefore carried out ab initio pseudopotential calculations<sup>7</sup> on the molecular and electronic structures of  $ScCp_2^+$  and  $LaCp_2^+$  and, for comparison, on  $MH_2^+$  and  $MF_2^+$  (M = Sc, La). While the isolated  $MCp_2^+$  cations are not known experimentally, such moieties are of considerable interest as fragments of the important  $Cp_2MX$  systems (e.g. X = halogen, hydride, alkyl, etc.).<sup>8,9</sup>

Figure 2 shows the bending potentials obtained for

(7) (a) Hartree-Fock gradient geometry optimizations and partial optimizations at the MP2 level of theory have been carried out with the Gaussian 90 program (Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90, Revision F; Gaussian, Inc., Pittsburgh, PA, 1990). For  $MCp_2^+$ , the SCF ring geometry obtained for the linear ( $D_{3d}$ ) metallocene structure was kept fixed in the partial optimizations of M-ring distances and ring-M-ring angles (within  $C_2$  symmetry) at the SCF and MP2 levels.  $MH_2^+$  and  $MF_2^+$  have been fully optimized within  $C_{2v}$  and  $D_{3h}$  symmetry. (b) Quasirelativistic 11-valence-electron pseudopotentials and extended valence spd basis sets have been used for Sc and La, augmented by one f function in MP2 calculations (Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* 1987, 86, 866. Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* 1989, 75, 173. Dolg, M.; Stoll, H. *Theor. Chim. Acta* 1989, 75, 369). Pseudopotentials and DZ valence basis sets have been used for C and F, with diffuse and polarization functions added on F (Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.* 1988, 65, 1321. Dolg, M. Dissertation, Stuttgart, Germany, 1989. Kaupp, M.; Stoll, H.; Preuss, H. *J. Comput. Chem.* 1990, 11, 1029. Cf. ref 6c for the fluorine basis.). A (4s)/[2s] hydrogen basis (Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3) was employed, with one p function ( $\alpha = 1.0$ ) added for  $MH_2^+$ .

(8) See, e.g.: Evans, W. J. *Adv. Organomet. Chem.* 1985, 24, 131.

**Table II.** Other Geometry Parameters<sup>a</sup> Calculated for  $MCp_2^+$  (M = Sc, La)<sup>7</sup>

M	R-MC	R-CC	R-CH	$\varphi$
Sc	2.477	1.411	1.065	4.3
La	2.880	1.410	1.066	6.0

<sup>a</sup>Distances in Å and  $\varphi$  in deg. The SCF results were obtained for linear ( $D_{3d}$ ) geometries. Cf. Figure 1 for the internal coordinates.

$MCp_2^+$ .<sup>7</sup> Table I gives the X-M-X angles, the linearization energies, and the M-X distances for  $MX_2^+$ . Table II summarizes the Cp ligand geometry. Obviously, all of these species are bent. As electron correlation is important for the quantitative evaluation of the angles and linearization energies (as well as for the M-ring distances in the metallocenes<sup>5</sup>), we will discuss only the MP2 results: The linearization energies for a given metal decrease along the series X = H, F, Cp, in agreement with an increasing  $\pi$ -bonding character of the ligand.<sup>5,6d,10</sup> However, even the  $MCp_2^+$  cations are considerably bent, in contrast to the floppy neutral  $MCp_2$  species (M = Ca, Sr, Ba, Sm, Eu, Yb).<sup>5</sup> The La systems are generally more strongly bent than the cations containing the smaller Sc.

Table III shows that  $\pi$  bonding dominates the covalent bonding contributions in the  $MCp_2^+$  systems (cf., for example, metal  $d_{xz}$  and  $d_{yz}$  populations). However, the  $\sigma$  populations (s and totally symmetric  $d_{z^2} + d_{x^2-y^2}$  populations) are by no means negligible. More importantly, the  $d_{z^2} + d_{x^2-y^2}$  populations increase considerably upon bending, leading to larger overall covalent bonding contributions (the average Sc-C Wiberg bond order increases from 0.166 to 0.173). The  $\pi$  populations change only very little. Thus, the  $\sigma$ -bonding contributions are responsible for the bent metallocene structures, even though they represent only a minor fraction of the total covalent bonding. This conclusion is likely to apply to the only slightly bent, more ionic  $MCp_2$  systems (e.g. M = Ba, Sm)<sup>5</sup> as well. Other cationic  $d^0$   $MCp_2^+$  (M = Y, Ln(III)) species are expected to adopt angles and linearization energies intermediate between  $ScCp_2^+$  and  $LaCp_2^+$ .

One aspect that could not be quantified in the present study is the magnitude of the ring-ring repulsion. While the smaller size of the group 3 trications compared to that of the group 2 and lanthanide(II) dications will increase the repulsion (and the polarization) of the rings, the smaller negative ligand charge in the  $MCp_2^+$  systems (e.g., the NPA charges are ca. 0.5 electron per Cp ring in  $ScCp_2^+$  compared to ca. 0.9 electron in  $CaCp_2^5$ ) will reduce it. As the square of the charges enters a Coulomb-type interaction law, the net effect probably is a reduction of the in-

(9) Semiempirical EHMO calculations predict a small preference for a bent structure in  $SmCp_2^+$ : Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* 1985, 24, 2095.

(10) Jolly, C. A.; Marynick, D. S. *Inorg. Chem.* 1989, 28, 2893.

(11) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* 1985, 83, 735.

Table III. Metal Valence Populations<sup>a</sup> for ScCp<sub>2</sub><sup>+</sup> in Different Geometries<sup>b</sup>

$\angle\text{CpScCp}$ , deg	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>	d <sub>xy</sub>	d <sub>zz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub> + d <sub>z<sup>2</sup></sub>	d <sub>tot</sub>
180	0.134	0.016	0.016	0.003	0.005	0.379	0.379	0.062	0.826
160	0.133	0.015	0.012	0.004	0.015	0.377	0.382	0.100	0.874

<sup>a</sup> Natural population analysis was employed.<sup>11</sup> <sup>b</sup> The yz plane contains the Cp ring midpoints and the metal.

ter-ring repulsion. This will also contribute to the more bent structures for the MCp<sub>2</sub><sup>+</sup> cations studied here compared to the neutral MCp<sub>2</sub> systems.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chem-

ischen Industrie, the Stiftung Volkswagenwerk, and Convex Computer Corp. M.K. acknowledges a Kékulé scholarship by the Fonds der Chemischen Industrie. We also thank Prof. H. Stoll (Stuttgart, Germany) for valuable suggestions.

OM9202377